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STRIPPING OF H_3PO_4 FROM NC4 – NC7 ALCOHOLS LOADED WITH PHOSPHORIC ACID

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Abstract

Pure phosphoric acid is obtained for food purposes by reduction of the phosphate rocks in an electric furnace to obtain P_2O_5 by the dry method. However, this method consumes a lot of energy and so it is rather expensive. There has been an increased interest in the past few years in purifying commercial wet phosphoric acid to obtain a pure acid. Several methods were developed on the pilot plant or commercial scales but most of the works are still in the developmental stage.

This paper studies stripping of H_3PO_4 from nC4 – nC7 alcohols loaded with phosphoric acid. The alcohol mainly used is n-heptanol. The effect of temperature and mixing time on distribution ratio were studied. The results show that the stripping increases by increasing the number of carbon atoms or the molecular weight of the n-alcohol and with n-C7 alcohol the stripping process has a higher efficiency. It was possible to obtain 85 % yield of H_3PO_4 by one stripping stage at room temperature. The temperature has a slight negative influence on stripping. The stripping is enhanced by increasing the concentration of P_2O_5in the loaded n-heptanol.

Keywords: phosphoric acid, alcohols, extraction, purification, stripping.

1. Introduction

In our earlier paper [1] we have studied the liquid-liquid extraction of H_3PO_4 by nC4 – nC7 alcohols. We found that the extraction decreases by increasing the number of carbon atoms or the molecular weight of the n-alcohol, but phase separation is slower. The alcohol mainly used for extraction is n-heptanol and we have found that the temperature has a slight negative influence on extraction. The extraction is enhanced by increasing P_2O_5 and alcohol concentrations. In this paper we will continue to study the stripping of H_3PO_4 from loaded alcohol by distilled water and the loaded alcohol mainly used is n-heptanol.

Purification of wet phosphoric acid was studied by DAVISTER [2], by liquid-liquid extraction with a mixture of diisopropylether DIPE and tributylphosphate TBP in kerosene diluent. Two thirds of P_2O_5 were extracted in 4 counter current stages at $5 - 25$ °C. The pure phosphoric acid was recovered from the solvent by stripping with distilled water under higher temperatures. The color was adjusted by active carbon.

CUER and FLOREANCIG [3] stated that P_2O_5 could be extracted by trioctylamine TOA but with more difficulty. Alcohols could also be used with higher selectivity for higher molecular weights. Ethers such as DIPE, DNPE di-(normal-propyl)ether could also be used at low temperatures of $5 - 25°C$. Phosphoorganic solvents could be used to extract P_2O_5 from wet phosphoric acid especially TBP since it has a low solubility in water and it is a common solvent. A mixture of TBP and DIPE in kerosene was used in a Ugine-Kuhlman pilot plant.

MCCULLOUGH [4] mentioned that Occidental Oil developed a process to extract H_3PO_4 from wet phosphoric acid by liquid-liquid extraction using n-heptanol. The acid was then stripped from the solvent by contact with distilled water. It was possible to remove 97% of the metals and 82% of the fluoride. Oxidation was used to remove the color of the acid.

BIERMAN [5] extracted H_3PO_4 from wet phosphoric acid by a high molecular weight hydrophobic alcohol such as hexanol. For extracting the metallic impurities a low molecular weight hydrophilic alcohol such as methanol was used. The mixture was separated into two phases. One phase consists of hexanol with pure H_3PO_4 and the other a methanol phase which is rich in metallic and anionic impurities. MEAB report [6] describes processes to purify wet phosphoric acid using partially immiscible solvents such as alcohols, ketones, ether and esters. The rejection of cationic impurities is marked and when operating with a concentarted feed acid the selectivity is poor. When ethers are selected as solvent, the effect of temperature is very important while with alcohols and ketones, it is not important.

2. Experimental

2.1. Materials

Normal aliphatic alcohols n-C4 to n-C7 from BDH with 99% wt purity were used. A commercial wet phosphoric acid from the General Fertilizer Company GFC Homs /Syria with 36.5% wt P_2O_5 and a specific gravity of 1.392 was used after being treated from solids and organics in the pilot plant for extraction of uranium.

2.2. Apparatus and Procedures

Extraction and stripping was carried out in a beacher with a magnetic stirrer placed in a thermostat to control the temperature. The aqueous and organic phases were stirred for 5 minutes and were allowed 20 minutes to separate in a funnel. The concentration of the acid was measured by a potentiometric titration with 0.1 NaOH. The potentiometer type of the E536 from Metrohm Co was used. The yield (Y) was calculated from the equation:

$$Y\% = \{[P_2O_5] \text{ loaded solvent } - [P_2O_5] \text{ barren solvent }\} / [P_2O_5] \text{ loaded solvent} \tag{1}$$

The distribution ratio (D) was calculated from the equation:

$$D = [P_2O_5] \text{ aqueous } / [P_2O_5] \text{ solvent} \qquad (2)$$

3. Results & Discussions

3.1. Effect of the Number of Carbon Atoms of Alcohols on Extraction and Stripping

The effect of the molecular weight of the n-alcohol on the liquid-liquid extraction system of wet phosphoric acid–alcohol–water was investigated. Wet phosphoric acid (P_2O_5 = 36.5% wt) was mixed with different alcohols from n-C4 to n-C7 without diluent under the same experimental conditions ($T = 25$°C, O/A = 5/1). The results are plotted in *Fig. 1* in the form of D and Y versus number of carbon atoms of the solvent. It is clear that extraction, as expected, decreases rapidly with the increase in the molecular weight or the number of carbon atoms of the solvent.

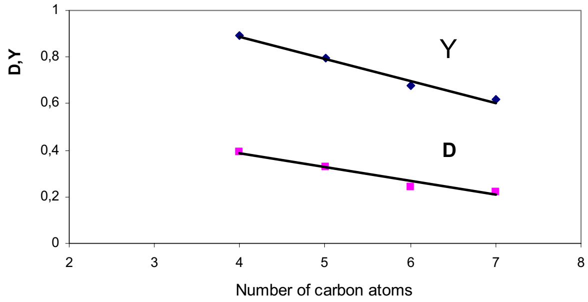

Fig. 1. Effect of molecular weight of n-alcohol on extraction of H_3PO_4 (P_2O_5 = 36.5% wt, O/A = 5/1, T = 25 °C)

Then, pure phosphoric acid was recovered by distillated water from different alcohols which loaded with P_2O_5 18 %wt. The results are plotted in *Fig. 2* in the form of D and Y versus number of carbon atoms of the solvent. Unlike in the extraction, it is clear that stripping increases rapidly with the increase in the molecular weight. Although n-heptanol has lower extraction efficiency but the stripping of H_3PO_4 from loaded n-heptanol by distilled water has a higher efficiency. Moreover, the n-heptanol has lower solubility and higher stability [7]. So experiments were further carried out on n-heptanol only.

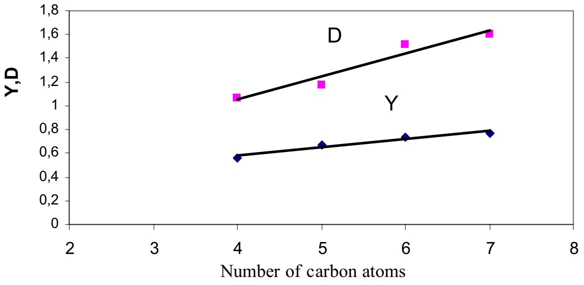

Fig. 2. Effect of molecular weight of n-alcohol on stripping of H_3PO_4
($P_2O_5 = 18\%$ wt, O/W = 2/1, $T = 25$ °C)

3.2. *Effect of Time of Mixing on Stripping*

The effect of time of mixing on stripping was investigated. The stripping was carried out by mixing distillated water with loaded n-heptanol under the conditions ($P_2O_5 = 8\%$ wt, O/W = 2/1, $T = 25$ °C). The time of mixing was varied from 30 to 180 seconds. The results are represented in *Fig. 3* in the form of D versus time of mixing. The results show that D increases very slightly from a value of 15.5 at 30 seconds to 16.2 at 90 seconds and remains constant after that. This shows that the reaction is rapid and diffusion which is influenced by stirring has very little influence on stripping. The mixing time was fixed at 5 minutes for other experiments.

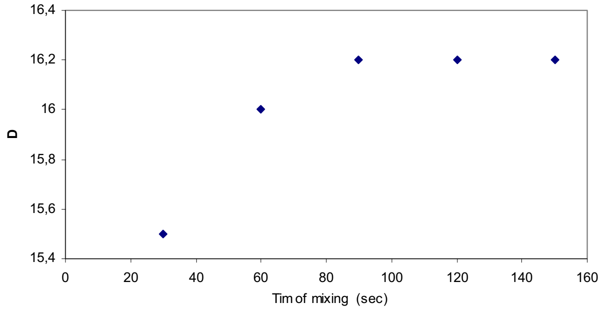

Fig. 3. Effect of time of mixing on stripping
($P_2O_5 = 8\%$ wt, O/W = 2/1, $T = 25$ °C)

3.3. Determination of the Stripping Isotherm

The stripping isotherm of H_3PO_4 by distillated water from n-heptanol ($P_2O_5 = 20\%$ wt) loaded with pure phosphoric acid was determined. The stripping was carried out under the conditions ($T = 25\,°C$, $P_2O_5 = 20\%$ wt). The results are shown in *Fig. 4* where P_2O_5% in the barren solvent is plotted versus P_2O_5% in the water.The experiment was repeated under the same temperture but for n-heptanol (8% wt. P_2O_5) loaded with wet phosphoric acid treated from solids only. The results are represented also in *Fig. 4* for comparison. From this figure we find that the first four points of each isotherm curve represent a straight line with a slope value of 7.13 for n-C7 loaded with wet H_3PO_4 and 2.89 for n-C7 loaded with pure H_3PO_4. These relatively high values confirm that the stripping is easier than extraction. *Fig. 5* and *Fig. 6* show the McCabe & Thiele diagrams [8] for stripping of H_3PO_4 from n-heptanol loaded with pure and wet H_3PO_4, respectively, by distillated water at phase ratio O/A = 2/1.

This method, as illustrated, shows that one stage is enough to give 85% stripping yield and to reduce the P_2O_5 content in the solvent to less than 2% for n-C7 loaded with pure phosphoric acid and to less than 0.5% for n-C7 loaded with wet phosphoric acid. This result is identical to the operation of a stripping unit in a commercial plant.

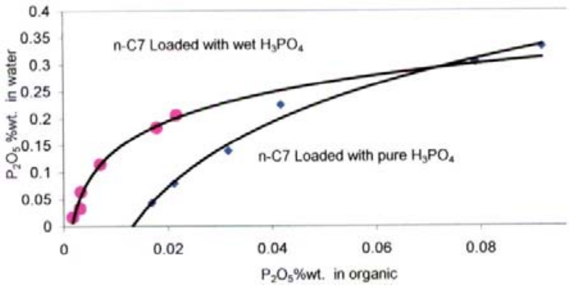

Fig. 4. Stripping isotherm of H_3PO_4 from n-C7
($P_2O_5 = 8\%$ wt, $P_2O_5 = 20\%$ wt, $T = 25$ °C)

3.4. Effect of Temperature on Stripping

The effect of temperature was investigated by stripping H_3PO_4 from loaded n-heptanol 10 % wt. P_2O_5 by distillated water using a phase ratio O/W = 2/1 but varying the temperature from 15 to 50 °C. The results are plotted in *Fig. 7* in the form of D versus T. The results show that temperature has a slight negative effect on the stripping of H_3PO_4 from loaded n-heptanol by distillated water. Therefore it is usual practice to carry out the stripping at room temperature.

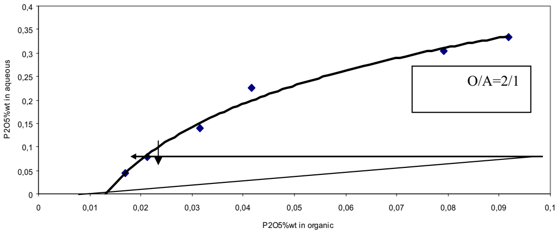

Fig. 5. Number of stages for stripping of H_3PO_4 from n-heptanol loaded with pure phosphoric acid by McCabe&Thiele method

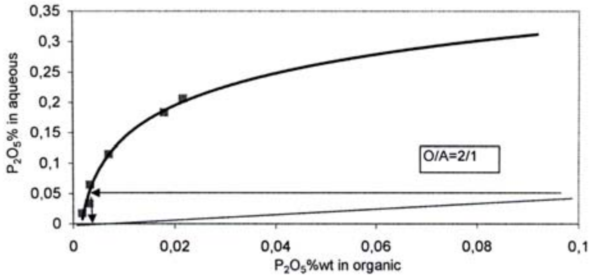

Fig. 6. Number of stages for stripping of H_3PO_4 from n-heptanol loaded with wet phosphoric acid by McCabe&Thiele method

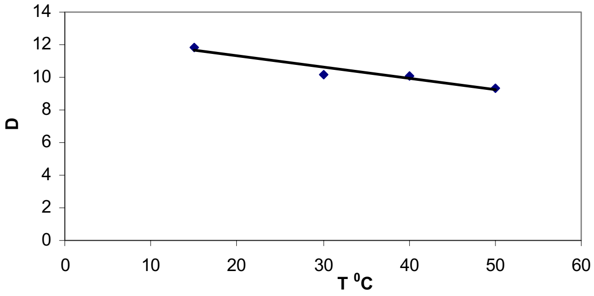

Fig. 7. Effect of temperature on stripping of H_3PO_4 from n-C7
($P_2O_5 = 10\%$ wt, O/W = 2/1)

3.5. Effect of Loaded n-heptanol Concentration

The effect of concentration of P_2O_5 in the loaded n-heptanol on stripping was studied by varying the concentration of P_2O_5 from 10 % wt to 18 % wt P_2O_5, while keeping other conditions constant ($T = 25\,°C$, O/W = 2/1). The results are shown in *Fig. 8* where the distribution ratio (D) and yield (Y) are plotted versus the concentration of P_2O_5% in the loaded n-heptanol. It is clear that the stripping increases by increasing the concentration of P_2O_5 in the loaded n-heptanol.

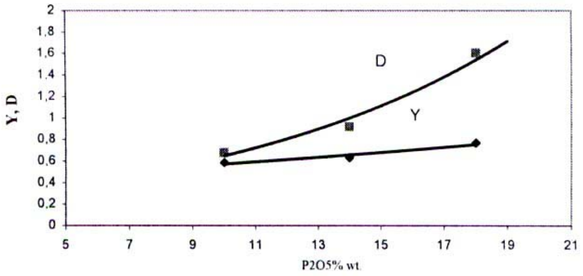

Fig. 8. Effect of P_2O_5 concentration in n-heptanol on stripping (O/W = 2/1, $T = 25$ °C)

3.6. Separation Time of Phases

Stripping of H_3PO_4 was caried out by mixing loaded n-heptanol (20 % wt. P_2O_5) with distillated water for five minutes at 25 °C using a phases ratio O/W = 2/1 and then let phases to separate. The variation of height of the interface from the bottom of the coloumn was measured with time. The results are represented in *Fig. 9* in the form of height of the interface versus time. The results show that the height of the interface remains constant after 60 seconds and the phase separation is very quick.

4. Conclusions

The previous results show that :

1. Unlike the extraction, stripping of H_3PO_4 from loaded n-alcohols by distillated water increases rapidly with the increase in the molecular weight or number of carbon atoms of the n-alcohols. The n-heptanol has lower solubility and higher stability so loaded n-heptanol is used as a compromise.
2. The temperature has a small negative effect on the stripping so stripping could be carried out at ordinary temperatures.

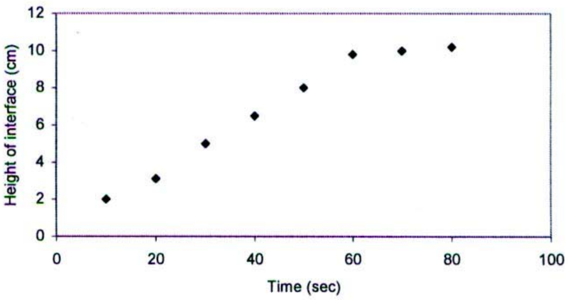

Fig. 9. Phase separation of stripping H_3PO_4 from n-heptanol ($P_2O_5 = 20\%$ wt, O/W = 2/1, $T = 25$ °C)

3. The time of mixing has a small effect on stripping which indicates that stripping is not diffusion controlled.
4. The concentration of loaded n-heptanol has a positive effect on the stripping so it is recommended to use loaded solvent with high concentration of P_2O_5.

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References

[1] Khorfan, S. – Shino, O. – Wahoud, A., Extraction of H_3PO_4 from Wet Phosphoric Acid by nC4 – nC7 Alcohols, *Periodica Polytechnica Ser. Chem. Eng.*, **45** No. 2 (2001), pp. 139–148.
[2] Davister, A. – Peeterbroeck, M., *Chem Eng Prog,* March (1982), p. 35.
[3] Floreancig, A. – Cuer, J. P., *Proceedings of the Second International Congress on Phosphorous Compoundes*, Boston (1980), Inst Mondial du phosphates, Paris (1981), p. 529.
[4] McCullough, J. F., *Chem Eng,* Dec 6 (1976), p. 101.
[5] Bierman, L. W. – Lopez, M. L. – Perkins, J. E., Purification of Phosphoric Acid, *United States Patent*, No. 4, 877, 594 Oct 31 (1989).
[6] MEAB Metallextractio AB; Purification of Wet Phosphoric Acid with Solvent Extarction, report ALPIN233/1, Sweden, September (1992).
[7] MERCK Index, 11 ed, Merck & Co Inc. U.S.A (1989).
[8] Perry, R. H. – Green, D., *Perry's Chemical Engineers' Handbook,* Mc Graw-Hill Inc. New York (1984) pp. 15-1.